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(54) Bread improvers.

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(56) References cited:

EP-A- 338 452	WO-A-89/09813
DE-A- 1 947 113	FR-A- 2 555 602
GB-A- 787 225	GB-A- 1 216 556
US-A- 2 783 150	US-A- 3 512 992

CEREAL CHEMISTRY, vol. 66, no. 2, 1989,
pages 73-78, St. Paul, MN, US; C.S. GAINES
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CEREAL CHEMISTRY, vol. 45, no. 4, 1968,
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(73) Proprietor: UNILEVER N.V.
Weena 455

NL-3013 AL Rotterdam (NL)

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(73) Proprietor: UNILEVER PLC
Unilever House
Blackfriars
P.O. Box 68
London EC4P 4BQ (GB)

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(72) Inventor: Maat, Jan
Molenstraat 2
NL-2681 BS Monster (NL)
Inventor: Roza, Martinus
Oolevaarstraat 9
NL-3291 XL Strijen (NL)

(74) Representative: Mulder, Cornelis Willem
Reinier, Dr. et al
UNILEVER N.V.
Patent Division
P.O. Box 137
NL-3130 AC Vlaardingen (NL)

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Cereal Chemistry, vol. 66 n 2, 1989, page 73*

Lebensm. Unters. Forsch. 84 178, 15-16

Derwent abstract 80-08549 C of JP 54160787

Kleffer, Zeitschrift für Lebensmittel Untersuchung und Forschung 173(5) 376 (1981)

Technical Information, Enzymes from miles,
additive DEEO

Abstract of * published in Cereal Chemistry,
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Description

This invention relates to additives for improving baked goods, particularly bread improvers, based on cellulolytic enzymes.

5 The term cellulolytic enzyme is generic for enzymes degrading cellulose. Examples of such enzymes are enzymes, that catalyze the hydrolysis of hexosepolymers such as cellulases and those, that catalyze the hydrolysis of pentose-polymers such as arabino-xylans, xylanases, arabinases and so forth. The addition to dough from which bakers goods are baked of such enzymes, usually in the commercial preparation as a mixture of several enzymes, provides improving effects such as increase in specific
10 volume, anti-staling improvement in crumb structure.

Although the addition of cellulolytic enzymes to bread is not permitted in various countries, they are in many cases present in the bread, because the amylases, which are permitted additives in bread making, contain these enzymes.

15 The presence of cellulolytic enzyme for example cellulase in alpha amylase comprising the active ingredient in a variety of enzyme-based bread improvers, gives rise to undesired side effects at higher concentrations used to provide these improvements in the greatest degree. In particular dough strength is reduced. The present invention proposes to overcome the disadvantage provided by the presence of cellulase in bread improver formulations by the inclusion of sufficient glucose oxidase and or peroxidase to inhibit its disadvantageous effects.

20 The invention may be applied as an additive with xylanase providing a mixture with other ingredients to be incorporated in dough for bread baking or for example in puff pastry dough.

The use of glucose oxidase as a bread additive has been already proposed in the form of ascorbic acid and/or reductic acid admixed with a glucose-oxidase-containing preparation together with inert fillers, to improve the baking qualities of flour and dough, the glucose-oxidase being extracted for instance from 25 moulds such as *A.niger*, described in British patent 787225. More recently, dough conditioners are described in USP 3392030 comprising dehydro forms of enediols of 3-ketoglycosides optionally admixed with glucose-oxidase to provide bread improver compositions, the glucose-oxidase providing for the preparation *in situ* of H₂O₂.

30 Food compositions such as dehydrated egg products, cereals and the like may be stabilised according to USP 2744017, by the addition of glucose oxidase to effect the removal of glucose, the presence of free oxygen to effect the enzymatic conversion of the aldose being proved by the inclusion of catalase together with a continuous addition of hydrogen peroxide.

35 Glucose oxidase is added together with cystine and catalase to bread dough according to a method for improving the quality of bread described in JP 57086235 and JP 57058844 and a comparison is made with the effect of adding calcium bromate and ascorbic acid, according to JP 57047434.

The effect of lipoxygenase and glucose oxidase on the rheological properties of dough are described in the abstract of the International Congress of Food Science and Technology (1978), page 235.

40 USP 3512992 describes an enzyme additive having pentosanase activity to improve resistance to staling, catalase being present to improve whiteness. German patent 2227368 also describes enzyme additives containing amylase, protease and pentosanase.

According to USP 3934040 an additive for standard doughs comprises cysteine ascorbic acid and fungal enzymes e.g. alpha amylase, protease, etc.

DE 26 15 392 describes a baking improver additive comprising cysteine, and ascorbic acid which may also contain hydrolase enzymes e.g. carbohydrazase or amylase.

45 Netherlands Patent 8401771 describes improving baking flours by increasing the enzyme activities of amylase, glucanase and xylanase in malt added to the flour.

In an article of P. Huhtanen c.s. in J. of Agricult.Sc. in Finland vol. 57 (1985) 284-292 the use of a mixture of cellulase and glucose oxidase as silage additive is described.

50 The invention is as defined in the claims.
The ratio of glucose oxidase or peroxidase to xylanase in bread improver compositions according to the present invention is not critical but the amount of glucose oxidase or peroxidase is preferably more than 1 ppm by weight of flour, preferably 1 to 10 ppm. 1 ppm corresponds with 125 units per mg. glucose oxidase or 210 purpurogallin units per mg peroxidase. The amount of additive expressed as final concentration on flour that may be used is preferably from 50 to 500 parts per million. Sufficient xylanase is preferably present to produce substantially maximum effect on specific volume.

55 The compositions contains preferably a sugar, in particular glucose as substrate for the glucose oxidase. Therefore the flour composition normally contains 0,05 - 5 wt% added sugar, preferably 0.1-2 wt% of added glucose.

The mixture of xylanase and glucose oxidase or peroxidase may be included in a bread improver composition containing further components, for example fat, additional enzymes, oxidising or reducing agents, sugars, emulsifiers, thickeners or gums and soya flour may be included. Additional enzymes may be included e.g. amylases, proteases, phospholipases and lipoxygenases.

5

EXAMPLE

A series of tests were conducted to compare the influence of glucose oxidase and horseradish peroxidase with xylanase on the stability of bread dough, prepared according to the following recipe:-

10

15

	Parts by weight
Wheat Flour	100
Yeast (compressed)	5
Water	58
Salt	2
Glucose	0.5 (substrate glucose oxidase)

20

The dough was mixed over 25 minutes in an Artofex mixer at 27°C. First and second proofs were conducted after 10 minutes each, with a final proof at 45 or 60 minutes. Bread rolls were prepared by baking the dough for 20 minutes at 240°C.

A series of samples were prepared as follows:

25

30

Sample		
A	xylanase 200 ppm	
B	xylanase 200 ppm	Glucose oxidase 1 ppm
C	xylanase 200 ppm	Glucose oxidase 2 ppm
D	xylanase 200 ppm	Horse Radish peroxidase 1 ppm
E	xylanase 200 ppm	Horse Radish peroxidase 2 ppm
Blank		

Both the dough and the baked rolls were tested. Results appear in the accompanying Table.

35

Dough property after mixing was soft and dry for all samples except the Blank which was tough and dry. After moulding, slight stickiness on the surface of the dough was observed only with the xylanase control (A) and the test with 1 ppm oxidase (B).

Dough softness was also exhibited after moulding by these two products, the remaining tests all being firm except for the blank which was tough.

40

The best stability was exhibited with the sample containing 2 ppm oxidase with the xylanase and this sample after baking also exhibited a more regular structure, better specific volumes and appearance for both final proof times than the remaining tests. In conclusion this sample has in all respects improved dough properties over the remainder.

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		Performance						
		Blank						
Time of sampling	Results on dough	Property						
		A	B	C	D	E	F	G
5	Directly after mixing (Kneading)	Workability	+	-	-	-	-	-
		Elasticity	+	-	-	-	-	-
10	Directly after molding	Stickiness	-	-	-	-	-	-
		Softness	-	-	-	-	-	-
15	Transport to oven	Stability	-	-	-	-	-	-
20								
25								
30								
35								
40								
45								
50								
	Results on product							
			Crust color	+	-	-	-	-
			Structure	-	-	-	-	-
			Volume (45')	5.31	5.24	5.35	5.10	5.17
			Volume (60")	4.86	4.73	4.87	4.57	4.64
			Appearance (45')	7	7	9	7	8
			Appearance (60")	4	4	6	5	5
								2

55 Claims

1. Flour composition incorporating a bread improver composition, containing amounts of cellulase and 1-10 ppm by weight of flour peroxidase corresponding with a peroxidase activity of 210-2100 purpurogal-

lin-units to achieve upon use in dough improved dough-strength, compared with a dough without the enzymes or containing only the cellulase.

2. Composition according to claim 1, comprising also 1-10 ppm oxidase corresponding with an oxidase activity of 125-1250 units glucose oxidase.
3. Composition according to claim 1 or 2 in which the composition also comprises an oxidase.
4. Composition according to claim 3, in which the oxidase is glucose oxidase.
5. Composition according to claims 1 to 3, in which the composition also comprises a sugar.
6. Composition according to claim 5 wherein the composition comprises glucose as the sugar.
7. Process for improving the dough strength from a dough by incorporation therein of a bread-improver composition, comprising higher concentrations of cellulase effective amounts of cellulase, 1-10 ppm on flour of, peroxidase, which peroxidase has an activity corresponding with 210 purpurogallin units per mg peroxidase, a sugar and optionally an oxidase.
8. Process according to claim 7, wherein the cellulase is xylanase.
9. Process according to claims 7 or 8, wherein the oxidase is applied in an amount of 1-10 ppm on flour.
10. Process according to claim 9, wherein the oxidase has an activity corresponding with 125 units per mg oxidase.
11. Process according to claims 7-10, wherein the flour applied, contains 0.05-5 wt% of added sugar, in particular glucose.

30 Patentansprüche

1. Mehlzusammensetzung, welcher ein Brotverbesserungsmittel einverleibt wurde, mit einem Gehalt an Cellulase und 1 bis 10 ppm, bezogen auf das Gewicht des Mehls, Peroxidase, entsprechend einer Peroxidaseaktivität von 210 bis 2100 Purpurogallin-Einheiten, zur Erzielung einer gegenüber einem nur die Cellulase enthaltenden Teig verbesserten Teigfestigkeit bei Verwendung in Teig.
2. Zusammensetzung nach Anspruch 1, die außerdem 1 bis 10 ppm Oxidase umfaßt, entsprechend einer Oxidaseaktivität von 125 bis 1250 Glucoseoxidase-Einheiten.
3. Zusammensetzung nach Anspruch 1 oder 2, wobei diese auch eine Oxidase umfaßt.
4. Zusammensetzung nach Anspruch 3, wobei die Oxidase Glucoseoxidase ist.
5. Zusammensetzung nach den Ansprüchen 1 bis 3, wobei diese auch einen Zucker umfaßt.
6. Zusammensetzung nach Anspruch 5, wobei diese Glucose als Zucker umfaßt.
7. Verfahren zum Verbessern der Teigfestigkeit eines Teigs, indem man diesem ein Brotverbesserungsmittel einverleibt, welches höhere Konzentrationen Cellulase, 1 bis 10 ppm, bezogen auf das Mehl, Peroxidase, wobei die Peroxidase eine 210 Purpurogallin-Einheiten pro mg Peroxidase entsprechende Aktivität aufweist, einen Zucker und wahlweise eine Oxidase enthält.
8. Verfahren nach Anspruch 7, bei dem die Cellulase Xylanase ist.
9. Verfahren nach einem der Ansprüche 7 oder 8, bei dem die Oxidase in einer Menge von 1-10 ppm, bezogen auf das Mehl, eingesetzt wird.

10. Verfahren nach Anspruch 9, bei dem die Oxidase eine 125 Einheiten pro mg Oxidase entsprechende Aktivität aufweist.
11. Verfahren nach einem der Ansprüche 7 bis 10, bei dem das eingesetzte Mehl 0,05-5 Gew.-% zugesetzten Zucker, insbesondere Glucose, enthält.
5

Revendications

1. Composition de farine incorporant une composition d'un améliorant pour le pain contenant certaines quantités de cellulase et 1 à 10 ppm de peroxydase en poids de farine correspondant à une activité de la peroxydase de 210 à 2100 unités de purpurogalline pour obtenir, lors de l'utilisation dans la pâte, une résistance de pâte améliorée, en comparaison avec une pâte à pain ne contenant que de la cellulase.
10
2. Composition selon la revendication 1, comprenant également 1 à 10 ppm d'oxydase correspondant à une activité oxydase de 125 à 1250 unités de glucose oxydase.
15
3. Composition selon la revendication 1 ou 2 dans laquelle la composition comprend également une oxydase.
20
4. Composition selon la revendication 3, dans laquelle l'oxydase est une glucose oxydase.
25
5. Composition selon les revendications 1 à 3, dans laquelle la composition comprend également un sucre.
30
6. Composition selon la revendication 5 dans laquelle la composition comprend du glucose comme sucre.
35
7. Procédé pour améliorer la résistance de la pâte à pain à partir d'une pâte en y incorporant une composition d'un améliorant pour le pain comprenant, des concentrations plus élevées de cellulase, 1 ppm à 10 ppm en poids de farine de peroxydase, laquelle peroxydase a une activité correspondant à 210 unités de purpurogalline par mg de peroxydase, un sucre et facultativement une oxydase.
40
8. Procédé selon la revendication 7, dans lequel la cellulase est de la xylanase.
45
9. Procédé selon les revendications 7 et 8, dans lequel l'oxydase est fournie dans une quantité comprise entre 1 ppm et 10 ppm en poids de farine.
50
10. Procédé selon la revendication 9, dans lequel l'oxydase a une activité correspondant à 125 unités par mg d'oxydase.
55
11. Procédé selon les revendications 7 à 10, dans lequel la farine fournie contient 0,05 % à 5 % en poids de sucre ajouté, en particulier du glucose.
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The compositions contains preferably a sugar, in particular glucose as substrate for the glucose oxidase. Therefore the flour composition normally contains 0,05 - 5 wt% added sugar, preferably 0,1-2 wt% of added glucose.

The mixture of xylanase and glucose oxidase or peroxidase may be included in a bread improver composition containing further components, for example fat, additional enzymes, oxidising or reducing agents, sugars, emulsifiers, thickeners or gums and soya flour may be included. Additional enzymes may be included e.g. amylases, proteases, phospholipases and lipoxygenases.

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A series of samples were prepared as follows:

25

	Sample	
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B	xylanase 200 ppm	Glucose oxidase 1 ppm
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D	xylanase 200 ppm	Horse Radish peroxidase 1 ppm
E	xylanase 200 ppm	Horse Radish peroxidase 2 ppm
Blank		

Both the dough and the baked rolls were tested. Results appear in the accompanying Table.

35

Dough property after mixing was soft and dry for all samples except the Blank which was tough and dry. After moulding, slight stickiness on the surface of the dough was observed only with the xylanase control (A) and the test with 1 ppm oxidase (B).

Dough softness was also exhibited after moulding by these two products, the remaining tests all being firm except for the blank which was tough.

40

The best stability was exhibited with the sample containing 2 ppm oxidase with the xylanase and this sample after baking also exhibited a more regular structure, better specific volumes and appearance for both final proof times than the remaining tests. In conclusion this sample has in all respects improved dough properties over the remainder.

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		Blank				
		A	B	C	D	
5	Directly after mixing (Kneading)	+ +	- -	- -	- -	ND
10			+	+	+	+
15			+	+	+	+
20			++	++	++	++
25						
30						
35						
40						
45						
50						
	PERFORMANCE					
	<u>Results on dough.</u>					
	<u>Times of Sampling</u>					
		Property	A	B	C	D
	Directly after mixing (Kneading)	Workability	+	+	+	+
		Elasticity	+	+	+	+
	Directly after molding	Stickiness	-	-	-	-
		Softness	-	-	-	-
	Transport to oven	Stability	-	-	-	-
	<u>Results on product</u>					
		Crust color	+	+	+	+
		Structure	-	-	-	-
		Volume (45')	5.31	5.24	5.35	5.10
		Volume (60")	4.86	4.73	4.87	4.57
		Appearance (45')	7	7	9	7
		Appearance (60")	4	4	6	5

55 Claims

1. Flour composition incorporating a bread improver composition, containing amounts of cellulase and 1-10 ppm by weight of flour peroxidase corresponding with a peroxidase activity of 210-2100 purpurogal-

lin-units to achieve upon use in dough improved dough-strength, compared with a dough without the enzymes or containing only the cellulase.

2. Composition according to claim 1, comprising also 1-10 ppm oxidase corresponding with an oxidase activity of 125-1250 units glucose oxidase.
3. Composition according to claim 1 or 2 in which the composition also comprises an oxidase.
4. Composition according to claim 3, in which the oxidase is glucose oxidase.
- 10 5. Composition according to claims 1 to 3, in which the composition also comprises a sugar.
6. Composition according to claim 5 wherein the composition comprises glucose as the sugar.
- 15 7. Process for improving the dough strength from a dough by incorporation therein of a bread-improver composition, comprising higher concentrations of cellulase effective amounts of cellulase, 1-10 ppm on flour of, peroxidase, which peroxidase has an activity corresponding with 210 purpurogallin units per mg peroxidase, a sugar and optionally an oxidase.
- 20 8. Process according to claim 7, wherein the cellulase is xylanase.
9. Process according to claims 7 or 8, wherein the oxidase is applied in an amount of 1-10 ppm on flour.
10. Process according to claim 9, wherein the oxidase has an activity corresponding with 125 units per mg oxidase.
- 25 11. Process according to claims 7-10, wherein the flour applied, contains 0.05-5 wt% of added sugar, in particular glucose.

30 Patentansprüche

1. Mehlzusammensetzung, welcher ein Brotverbesserungsmittel einverleibt wurde, mit einem Gehalt an Cellulase und 1 bis 10 ppm, bezogen auf das Gewicht des Mehls, Peroxidase, entsprechend einer Peroxidaseaktivität von 210 bis 2100 Purpurogallin-Einheiten, zur Erzielung einer gegenüber einem nur die Cellulase enthaltenden Teig verbesserten Teigfestigkeit bei Verwendung in Teig.
- 35 2. Zusammensetzung nach Anspruch 1, die außerdem 1 bis 10 ppm Oxidase umfaßt, entsprechend einer Oxidaseaktivität von 125 bis 1250 Glucoseoxidase-Einheiten.
- 40 3. Zusammensetzung nach Anspruch 1 oder 2, wobei diese auch eine Oxidase umfaßt.
4. Zusammensetzung nach Anspruch 3, wobei die Oxidase Glucoseoxidase ist.
5. Zusammensetzung nach den Ansprüche 1 bis 3, wobei diese auch einen Zucker umfaßt.
- 45 6. Zusammensetzung nach Anspruch 5, wobei diese Glucose als Zucker umfaßt.
7. Verfahren zum Verbessern der Teigfestigkeit eines Teigs, indem man diesem ein Brotverbesserungs-mittel einverleibt, welches höhere Konzentrationen Cellulase, 1 bis 10 ppm, bezogen auf das Mehl, Peroxidase, wobei die Peroxidase eine 210 Purpurogallin-Einheiten pro mg Peroxidase entsprechende Aktivität aufweist, einen Zucker und wahlweise eine Oxidase enthält.
- 50 8. Verfahren nach Anspruch 7, bei dem die Cellulase Xylanase ist.
- 55 9. Verfahren nach einem der Ansprüche 7 oder 8, bei dem die Oxidase in einer Menge von 1-10 ppm, bezogen auf das Mehl, eingesetzt wird.

10. Verfahren nach Anspruch 9, bei dem die Oxidase eine 125 Einheiten pro mg Oxidase entsprechende Aktivität aufweist.

5 11. Verfahren nach einem der Ansprüche 7 bis 10, bei dem das eingesetzte Mehl 0,05-5 Gew.-% zugesetzten Zucker, insbesondere Glucose, enthält.

Revendications

10 1. Composition de farine incorporant une composition d'un améliorant pour le pain contenant certaines quantités de cellulase et 1 à 10 ppm de peroxydase en poids de farine correspondant à une activité de la peroxydase de 210 à 2100 unités de purpurogalline pour obtenir, lors de l'utilisation dans la pâte, une résistance de pâte améliorée, en comparaison avec une pâte à pain ne contenant que de la cellulase.

15 2. Composition selon la revendication 1, comprenant également 1 à 10 ppm d'oxydase correspondant à une activité oxydase de 125 à 1250 unités de glucose oxydase.

20 3. Composition selon la revendication 1 ou 2 dans laquelle la composition comprend également une oxydase.

25 4. Composition selon la revendication 3, dans laquelle l'oxydase est une glucose oxydase.

30 5. Composition selon les revendications 1 à 3, dans laquelle la composition comprend également un sucre.

35 6. Composition selon la revendication 5 dans laquelle la composition comprend du glucose comme sucre.

40 7. Procédé pour améliorer la résistance de la pâte à pain à partir d'une pâte en y incorporant une composition d'un améliorant pour le pain comprenant, des concentrations plus élevées de cellulase, 1 ppm à 10 ppm en poids de farine de peroxydase, laquelle peroxydase a une activité correspondant à 210 unités de purpurogalline par mg de peroxydase, un sucre et facultativement une oxydase.

45 8. Procédé selon la revendication 7, dans lequel la cellulase est de la xylanase.

50 9. Procédé selon les revendications 7 et 8, dans lequel l'oxydase est fournie dans une quantité comprise entre 1 ppm et 10 ppm en poids de farine.

55 10. Procédé selon la revendication 9, dans lequel l'oxydase a une activité correspondant à 125 unités par mg d'oxydase.

60 11. Procédé selon les revendications 7 à 10, dans lequel la farine fournie contient 0,05 % à 5 % en poids de sucre ajouté, en particulier du glucose.

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